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SYNTHESIS OF $FeSb_2$ NANORODS AND NANOPARTICLES BY SOLVOTHERMAL SYNTHESIS ROUTES (BRIEFING CHARTS)

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Thermal Sciences and Materials Branch
Nonmetallic Materials Division

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14. ABSTRACT
FeSb2 has recently been considered as a novel thermoelectric material due to a Seebeck coefficient of ~-45000 µVK-1 and a thermoelectric power factor of ~2300 µWK-2 cm-l at low temperatures (Bentien, A. et al. 2007 *Europhys. Lett.* 80 17008). However, its thermoelectric potential is limited by a high thermal conductivity. To lower the thermal conductivity, both nanorods and nanoparticles of $FeSb_2$ were synthesized. Nanorods were synthesized following a previously published solvothermal synthesis in ethanol. Nanoparticles were synthesized using a novel sodium naphthalenide reduction in triglyme at ambient pressure. XRD was used to characterize both materials.

15. SUBJECT TERMS
thermoelectric material, nanorods, iron antimonide, solvothermal synthesis

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Synthesis of $FeSb_2$ Nanorods and Nanoparticles by Solvothermal Synthesis Routes

ACS Central Regional Meeting 2010

Dayton, OH

June 17, 2010

Thermal Sciences and Materials Branch

AFRL/RXBT

Materials and Manufacturing Directorate

Air Force Research Laboratory

Joel Schmidt

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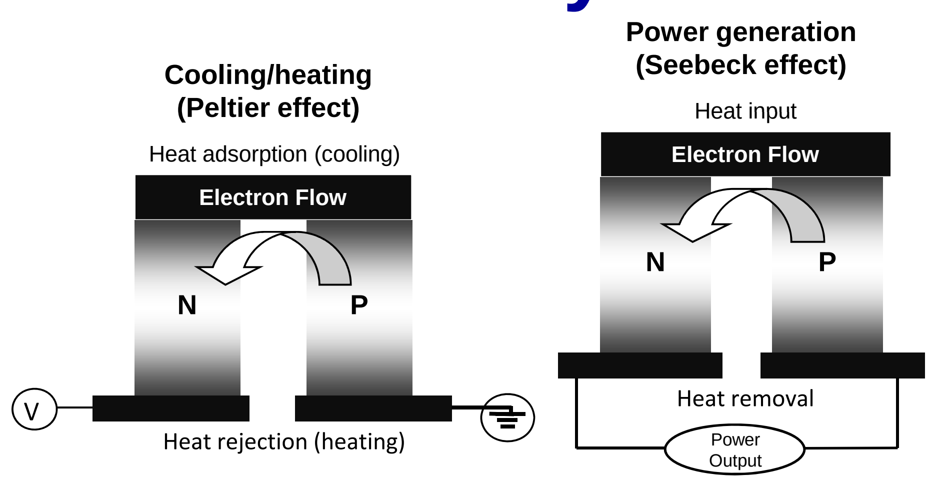
Thermoelectric Materials

- Durable solid state devices which provide cooling, power generation and waste heat harvesting
- Used on deep space probes, sensor cooling and small scale refrigeration
- Current work mostly concentrated on room temperature to high temperature
- Need for low temperature TE's for sensor cooling applications

Theory



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Increasing Efficiency

- Figure-of-Merit

$$ZT = \frac{\alpha^2 \sigma T}{\kappa}$$

- ZT drops off at low temperature
- ZT = 1 state of the art at room temperature

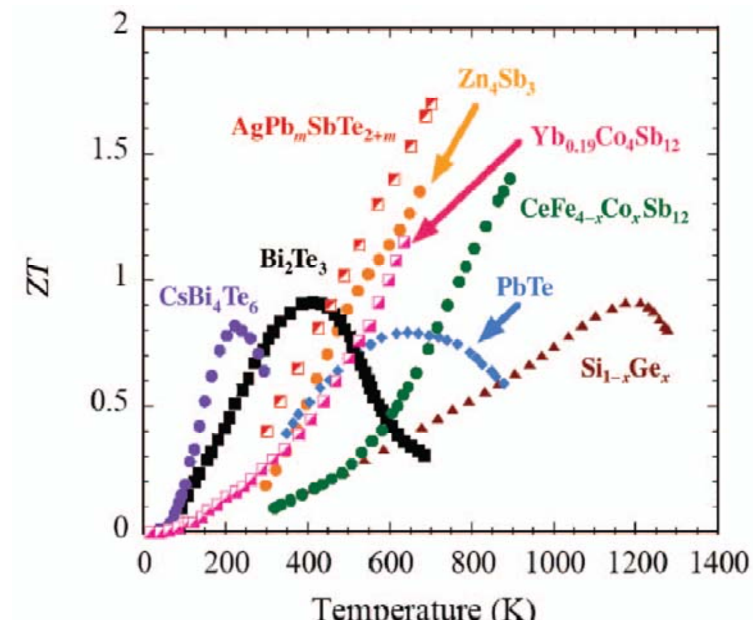
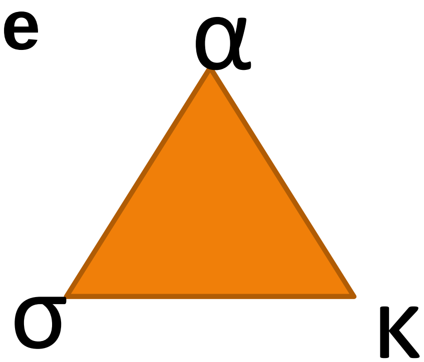


Fig. 1. Figure-of-Merit ZT as a Function of Temperature for Selected TE Materials (from Tritt & Subramanian)

Difficulty of optimizing three Interrelated parameters



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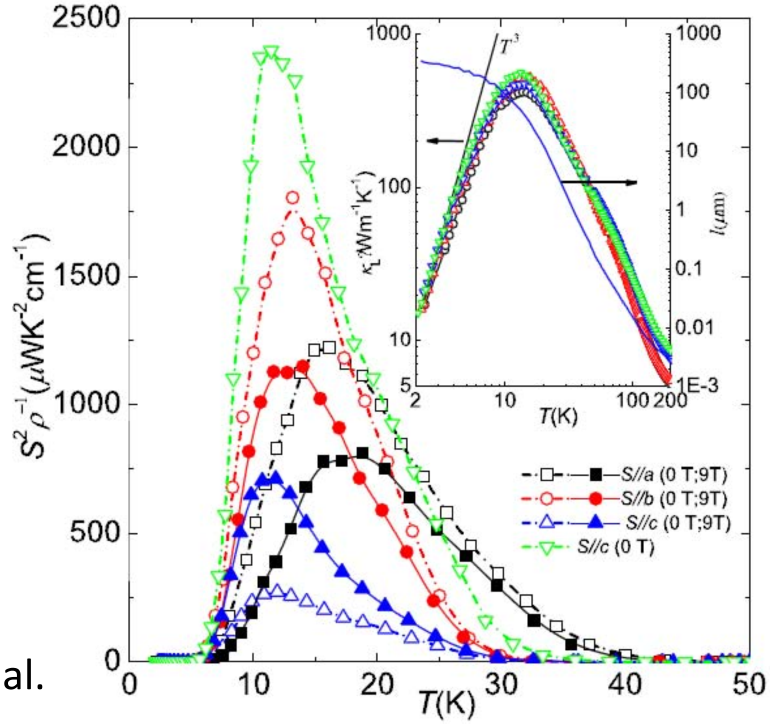
$FeSb_2$ Thermoelectric Power Factor

- **$FeSb_2$ is narrow gap semiconductor material**
- **Exhibits a huge Seebeck Coefficient of ~-45,000 µV/K at 10 K**
- **Has a record high thermoelectric power factor of ~2300 µW/K² at 12 K**
  - 65 times larger than that of Bi_2Te_3
  - Thermal conductivity of ~500 W/mK leads to a ZT ~ 0.005 at 12 K



A. Bentien et al.

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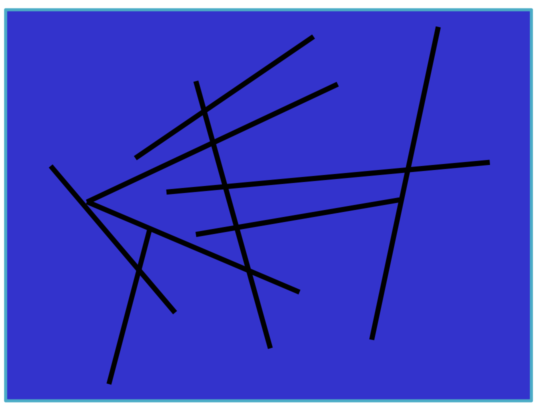
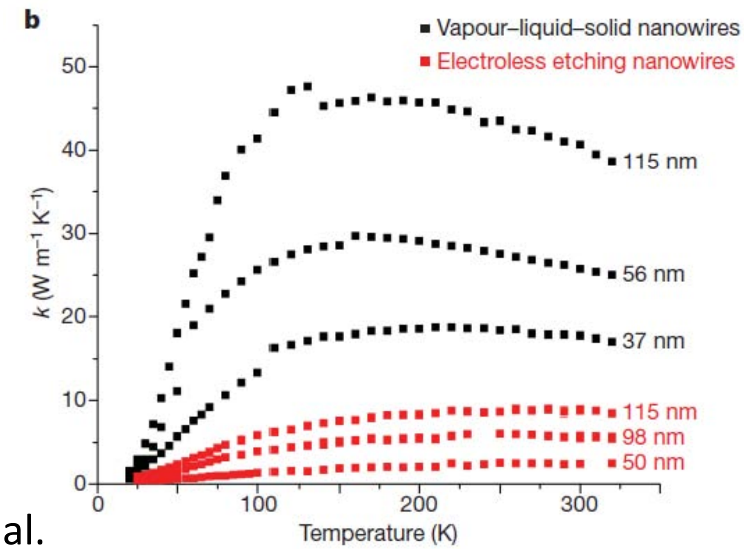
Thermal Conductivity Reduction

- Bouka et al. and Hochbaum et al. showed it was possible to greatly reduce the κ of silicon by synthesizing nanowires
- Preparing nanostructures with one of more dimension smaller than the mean free path of phonons but larger than the mean free path of electrons and holes can greatly reduce κ without decreasing σ
- Difficulty in preparing nanostructures!





Hochbaum et al.

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$FeSb_2$ Synthesis

- **Traditional alloying methods:**
  - Heat Fe and Sb to 1070 K for 1 day, crush then temper at 970 K for 7 days, crush then temper at 870 K for 21 days then cool (Gronvold et al.)
  - Melt using high-frequency induced current, anneal at 773 K for 7 days, ball-mill into fine powder (Xie et al., 2003)
- **Problems:**
  - Do not produce nanostructures
  - High temperatures and long synthesis times are impractical for large scale production

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Nanowire synthesis

- **Reported as a Li-Ion battery anode material**
- **Procedure (Xie et al., 2006):**
  - $FeCl_3$•$6H_2O$, $SbCl_3$, $NaBH_4$ and anhydrous ethanol were combined in a Parr pressure reactor and heated to 260 °C for 3 days
  - $NaBH_4$ quickly reduces $FeCl_3$ and $SbCl_3$ in the first two reaction so the longer reaction time is needed for the final alloying reaction:

$$FeCl_3 + 3NaBH_4 \rightarrow Fe \text{ to } 3/2H_2 + 3\ BH_3 + 3NaCl \qquad [1]$$

$$2SbCl_3 + 6\ NaBH_4 \rightarrow 2Sb + 3H_2 + 6BH_3 + 6NaCl \qquad [2]$$

$$Fe + 2Sb \rightarrow FeSb_2 \qquad [3]$$

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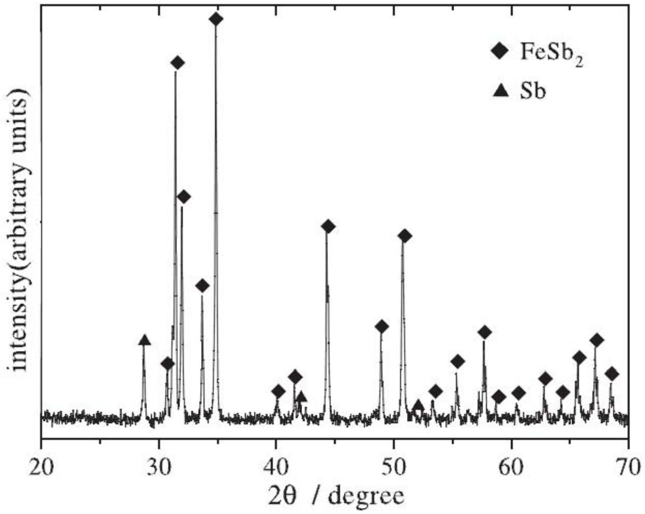
Product Characterization

- **XRD used for bulk powder characterization**

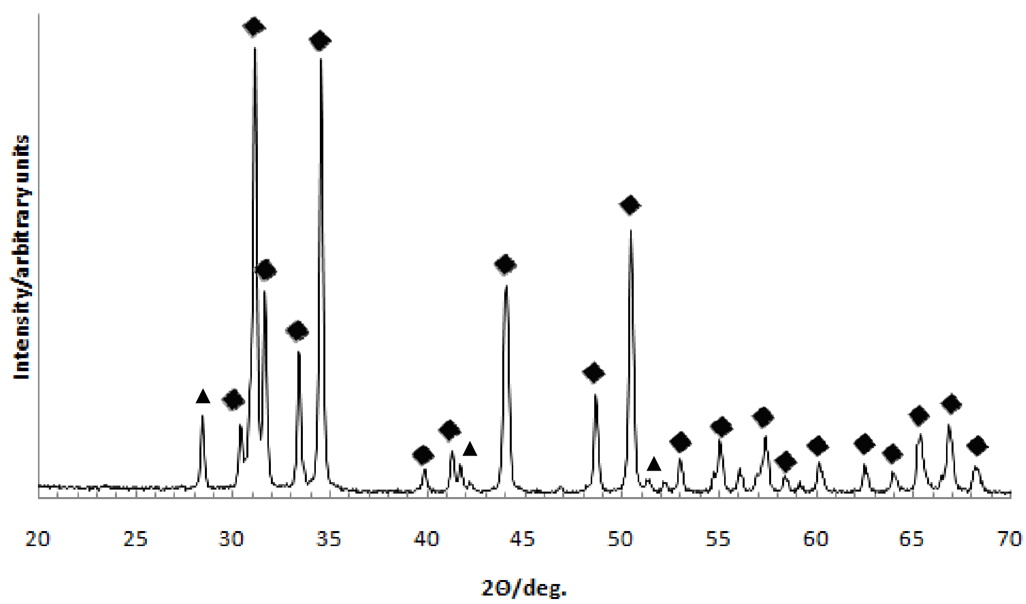


Xie et al., 2006

Experimental results

•Literature and experimental preparation compare closely

•Ran for 100 hours, predissolved all reagents



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Synthesis Challenges

- **$NaBH_4$ quickly reduces $FeCl_3$ and $SbCl_3$ and the alloying reaction takes place slowly**
- **Silver flakes of antimony metal were visible after the reaction each time it was run**
  - Confirmed by XPS
- **Excess iron metal could not be found**
- **Need to purify the product and remove unreacted antimony**

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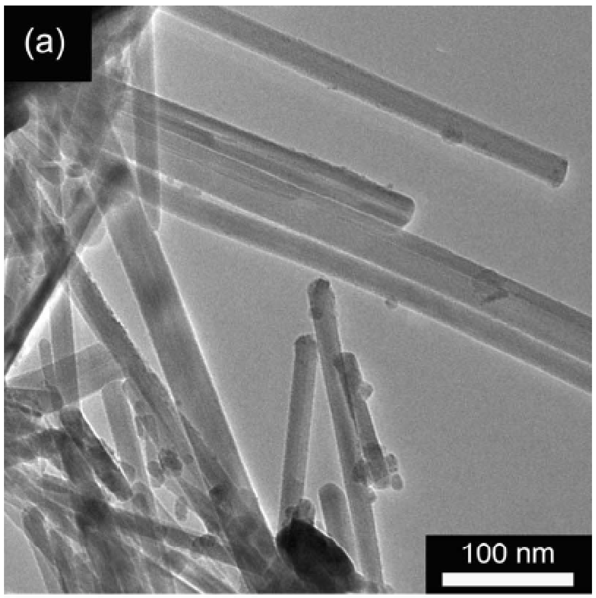
Nanorod characterization

- **Characterize nanorods by SEM and TEM**

Literature TEM



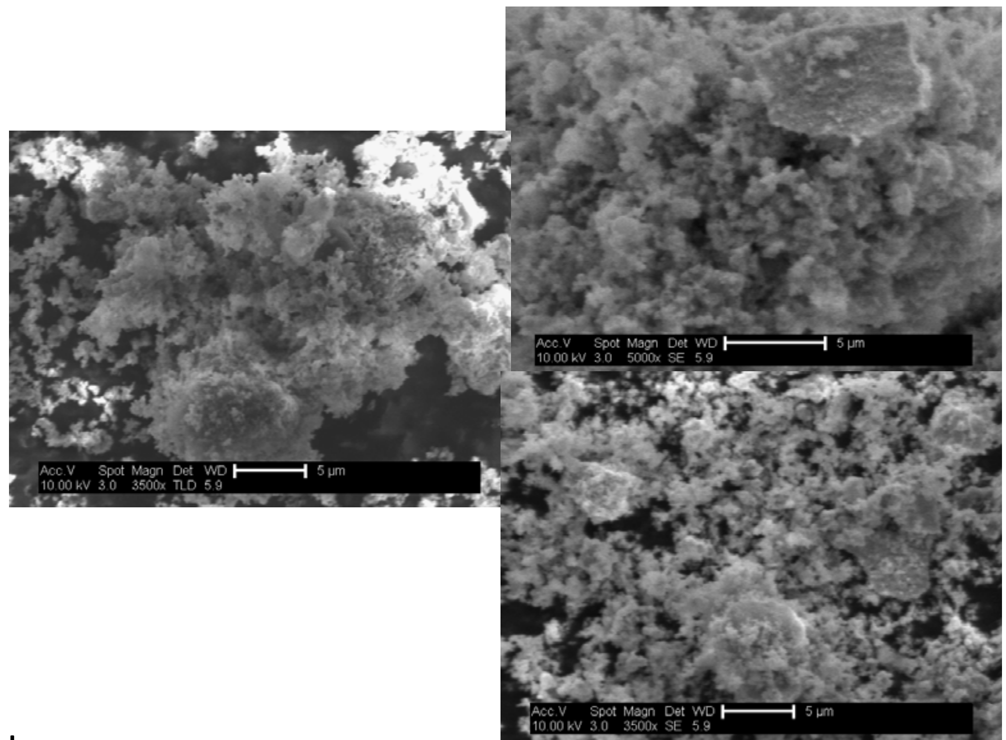
Nanorod size:

•Large nanorods 200-400 nm in length and 30-40 nm diameter

•Small nanorods 50-200 nm in length and 20-30 nm in diameter

(Xie et al.)

Experimental SEM



SEM shows much smaller particle size

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Nanoparticle Synthesis

- **Novel synthesis route using a sodium naphthalenide reduction**
  - Used in literature to prepare compounds such as:
    - PtPb (Alden et al.)
    - InSb (Cho and Lim)
    - GaP (Hwang et al.)
  - Possible reaction difficulties:
    - Rate of reduction needs to be diffusion-limited so that homogeneous particles are formed
    - Choice of solvent so that all materials are soluble
  - This method can be applied to a wide range of systems

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Procedure

$$\text{Na(s)} + \text{Naphthalene(s)} \xrightarrow[\text{Stir overnight}]{\text{Triglyme}} \text{Sodium Naphthalenide}$$

(2g) **(1g)** **(Dark green)**

$$\text{Sodium Naphthalenide} + FeCl_3 + SbCl_3 \xrightarrow[\text{2 hours}]{300\ ^\circ\text{C}} FeSb_2$$

(0.811 g) **(2.28 g)**

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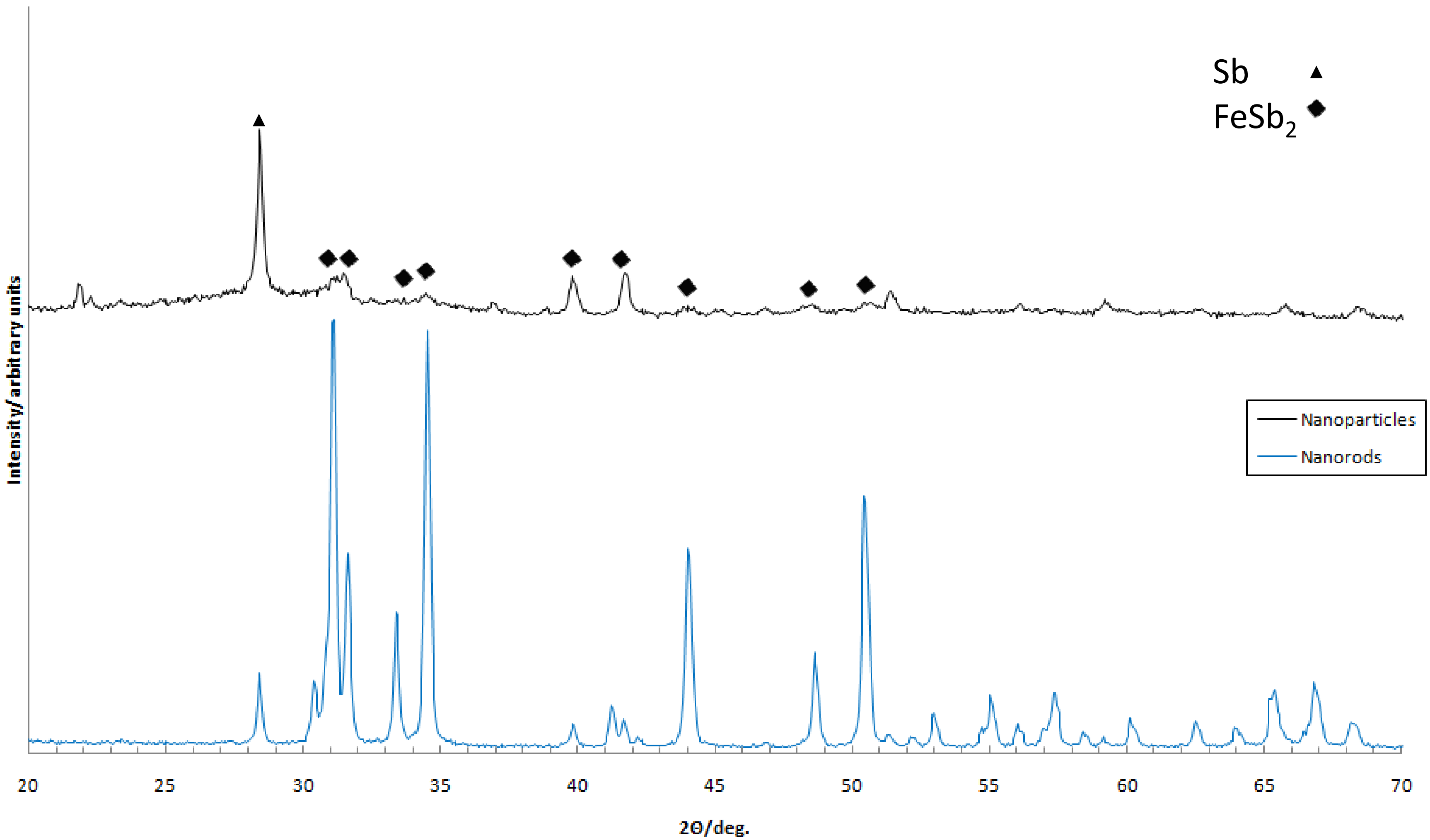
XRD Characterization



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XRD Conclusions

- **Small particle size leads to broader and less well defined peaks**
- **Presence of antimony metal is easily seen**
- **Product $FeSb_2$ is able to be seen in XRD but it has a very weak signal**
- **Need to perfect the synthesis method in order to get high purity nanoparticles**

Initial attempts to synthesize do appear to be successful!

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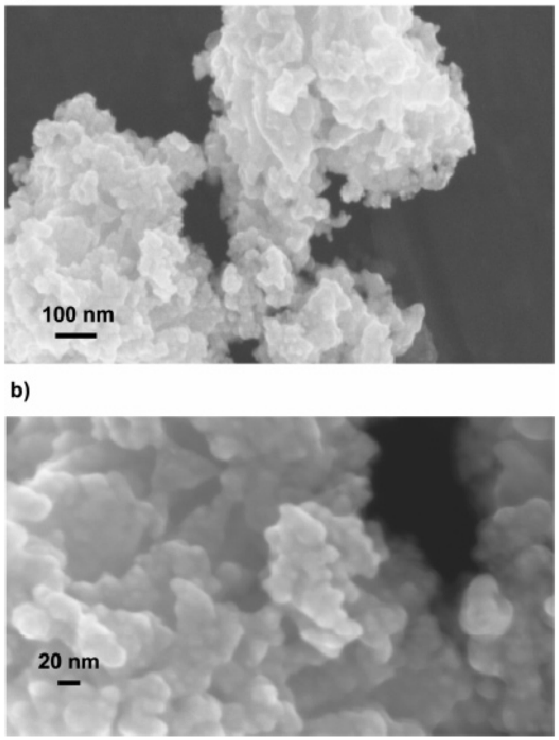
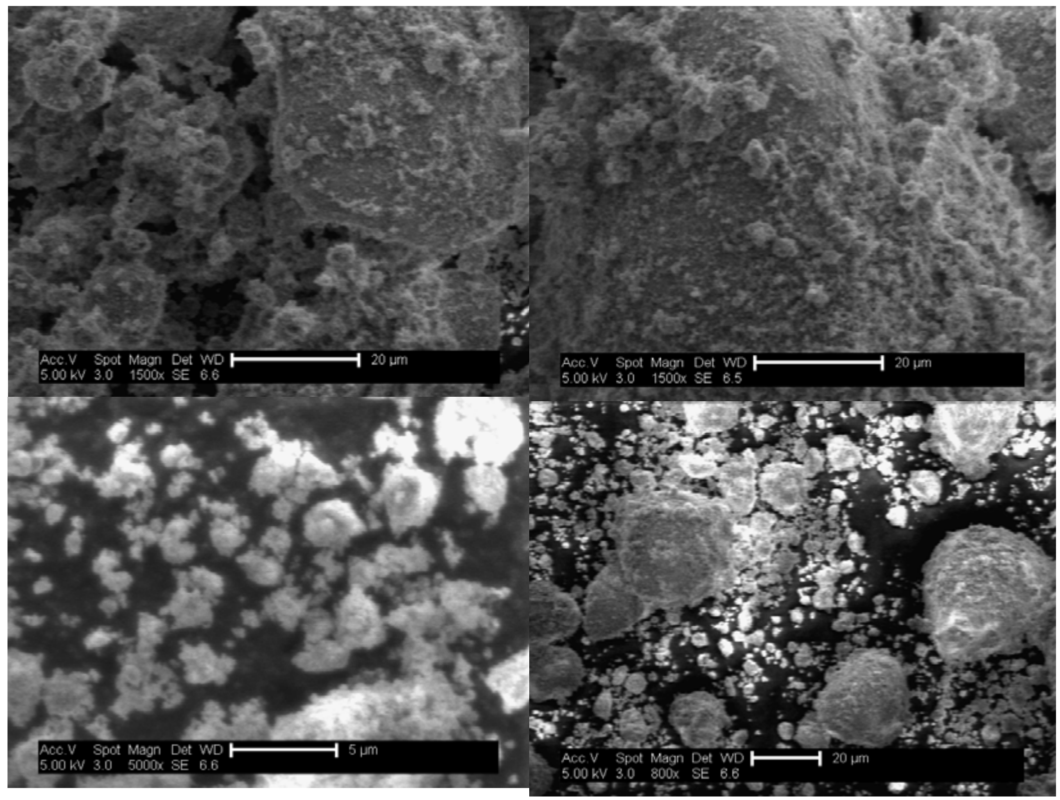
SEM Images

PtPb Nanoparticles



Shown for comparison of particle size and clustering
(Alden et al.)

FeSb Nanoparticles



The image shows the small particle size as well as clustering

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Summary of Experimental Results

- **Novel synthesis route utilizing a sodium naphthalenide reduction in trigylme at 300 °C and ambient pressure**
- **XRD shows that product has been formed, however it is contaminated**
- **SEM shows small particle size**
- **Need to optimize method for increased yields and purity**

Synthesis method is ideal for scale up since costly pressure vessels are not required and the reaction is on the order of hours instead of days

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Future Work

- Optimize both synthetic routes
- Use of surfactants to control nanorod length and diameter and nanoparticle size
- Increase purity and yield of reactions
- Scale up
- Transport property characterization at cryogenic temperatures
- Addition of impurities to increase electrical conductivity and decrease thermal conductivity

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Conclusions

- Successfully reproduced literature synthesis of $FeSb_2$ nanorods
- Initial characterization shows that a novel synthesis method of $FeSb_2$ nanoparticles has been developed
- Need to increase yields and purity
- Characterize cryogenic transport properties

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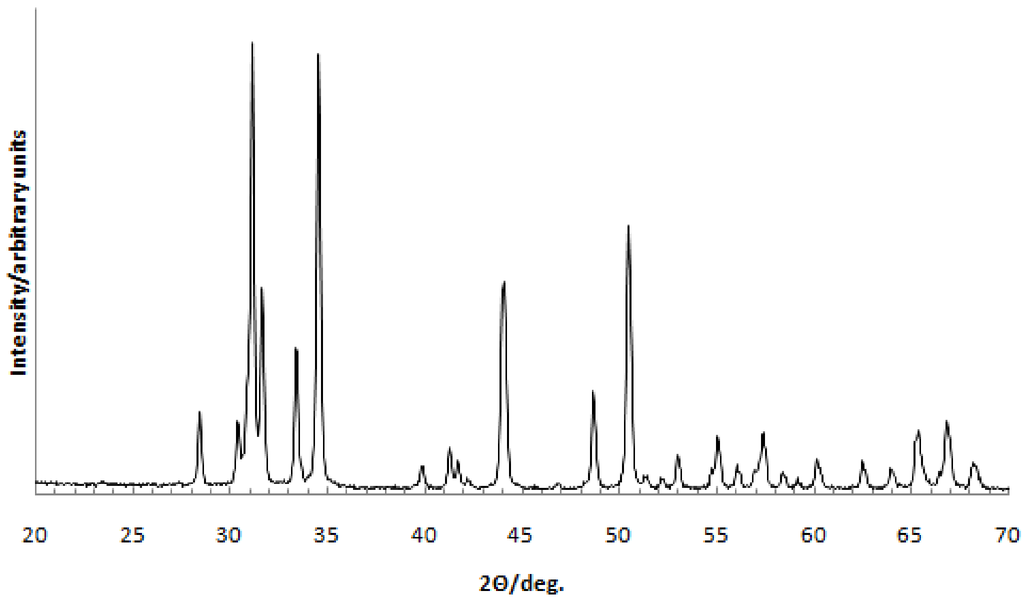

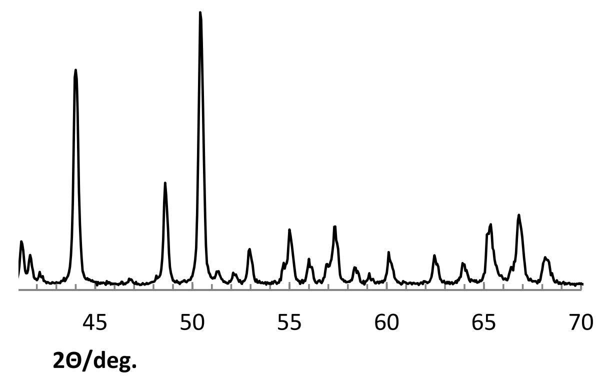

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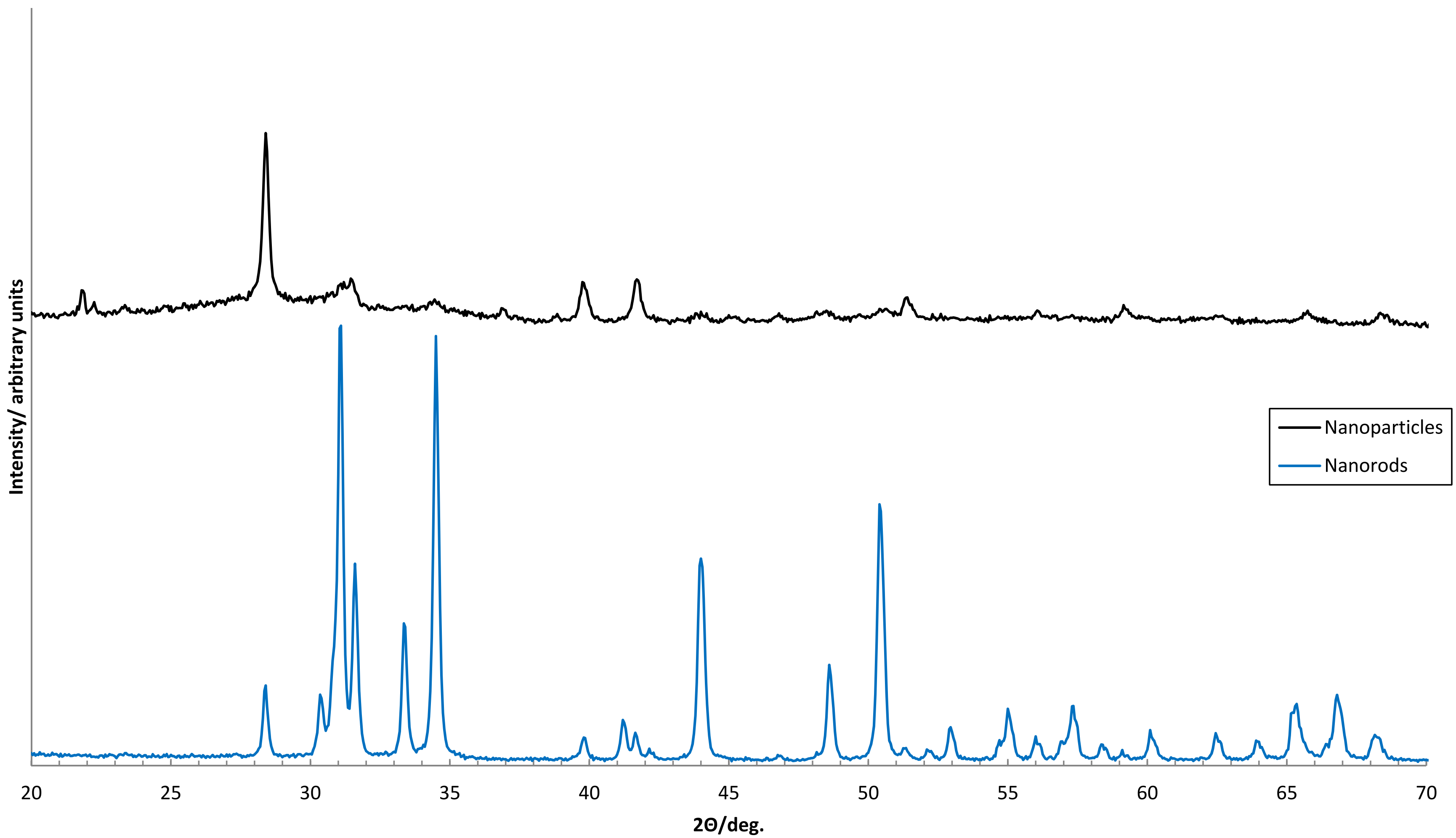

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